

NICKELIFEROUS NONTRONITE, A 15Å GARNIERITE, AT NIQUELANDIA, GOIÁS, BRAZIL

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Abstract—Garnierite from the Tocantins Complex at Niquelandia, Brazil, is a 15Å, dioctahedral clay mineral, nickeliferous nontronite. The principal octahedral cations are Fe^{3+} , Al and Ni. The ferric state of the iron has been verified by ESCA. Ni occupies both the octahedral site and an exchange site. The garnierite formed (and is still forming) by the weathering of nickeliferous pyroxenite. Although the garnierite is a secondary product of weathering, it undergoes further change as weathering progresses: Ni and silica decrease, Fe^{3+} and Al increase, and the color changes from bright yellow green to red brown. Eventual breakdown of the garnierite leaves mainly hydrated oxides of iron and aluminum.

OCCURRENCE AND APPEARANCE

In central Goiás (Fig. 1) a lense-shaped massif of basic and ultra-basic rocks called the Tocantins Complex (Pecora, 1944; Lindenmayer, Motta, Reis and Araujo, 1970) contains nickel-copper-cobalt deposits, associated with which are conspicuous outcrops of a bright green mineral which has been called 'garnierite', 'garnieritic clay' (Pecora, 1944; Berbert, 1970) or 'garnieritic or silicate ore' (Costa, 1970).

Excellent exposures of the garnieritic clay are in prospect pits of the Jacuba I ore body, overlying weathered pyroxenite (see Pecora, 1944, pp. 265-69 and Plate 47). From a distance, the clay is bright yellow-green (5GY 6/4) and appears to be fairly homogeneous. Close-up, it consists of small irregularly shaped masses and microveinlets of green clay and associated reddish to purplish clay, to which it is gradational. Both the green and the associated reddish clay are nickeliferous, containing 0.5-17% NiO. The predominant color of the garnierite is green and it comprises zones up to several meters thick in the upper part of the saprolite. At places the garnierite preserves the original texture and jointing of the pyroxenite from which it was derived, especially in the lower part of the weathering profile. Superimposed on the relict texture and commonly obliterating it are numerous textural heterogeneities caused by repeated shrinkage-expansion, slumping and color changes related to leaching and oxidation and near-surface weathering phenomena. Locally these develop spotting or mottling as conspicuous secondary textures. Near the bottom of the weathering profile, the green clay is found in the interstices of weathered pyrox-

enite and along small cracks. Minute veinlets of dark green clay commonly cut green clay of lighter hue. Toward the surface, the green clay is generally lighter colored, where its nickel has been partly leached.

From near-surface samples collected in August, 1973, a clean sample of the green garnierite was hand-picked under the binocular microscope for a chemical analysis and for X-ray and electron-optical examination. A sample of associated reddish clay was hand-picked for comparative examinations.

X-RAY EXAMINATION

X-ray powder diffraction patterns were recorded with a Norelco diffractometer using CuK_{α} radiation. A cell mount was used to obtain diffraction data on essentially unoriented material. A slurried sample sedimented onto glass slides was used for recording

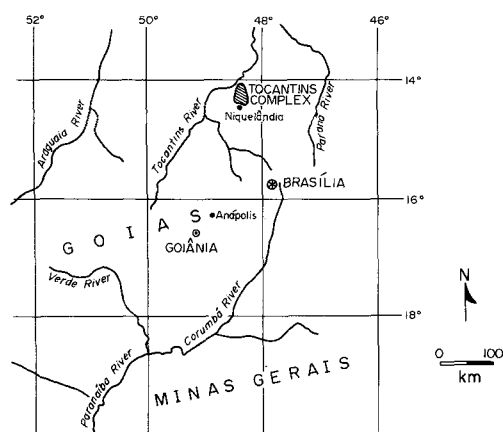


Fig. 1. Location of the Tocantins basic complex near Niquelandia, Goiás, Brazil.

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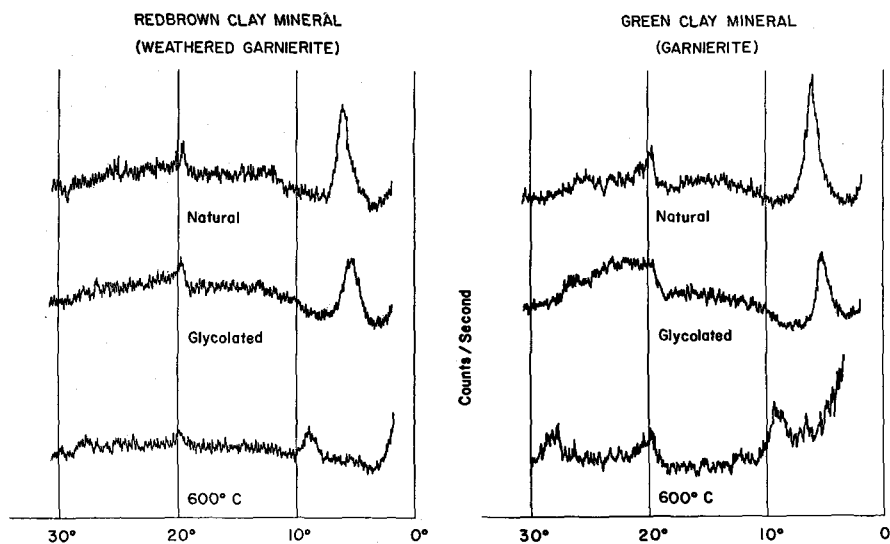


Fig. 2. X-ray powder diffraction patterns of garnieritic clay, Niquelandia, Brazil, CuK_α radiation, $2^\circ/\text{min}$ scan rate. Samples were sedimented onto glass slides. PHA was used to discriminate against secondary Fe fluorescence from the sample.

basal reflections before and after glycolation and heat treatment.

Only one crystalline mineral was detected in the hand-picked samples; smectite. The basal spacing of the natural green smectite is 14.8\AA ; glycolation expands it to 17\AA ; heating at 600°C for 15 min collapses it to about 9.5\AA . The corresponding diffraction patterns for the redbrown clay are similar (Fig. 2). The (060) spacing of both samples, measured on cell mounts with little preferred orientation, is 1.51\AA . The X-ray data indicate that the Niquelandia garnierite is a 15\AA clay mineral, a smectite, and it is essentially dioctahedral.

CHEMICAL EXAMINATION

The chemical composition of the green garnierite was determined by several methods. Procedures for silica, alumina, total iron, ferrous iron and total water were taken from Carmichael (1970). The combined gravimetric-photometric procedure for silica determination has been described by Jeffery and Wilson (1960, pp. 478–85). The method used to determine ferrous iron has been described by Wilson (1960, pp. 823–27). NiO was gravimetrically determined according to the procedure of Jeffery (1970, pp. 336–38). Atomic absorption spectroscopy was used for CaO and MgO; flame emission spectroscopy was used for Na_2O and K_2O . X-ray fluorescence emission gave TiO_2 and MnO as well as a check on silica and alumina. Total water was determined gravimetrically by the Penfield tube method, with sodium tungstate as flux.

The cation exchange procedure was that of Mungan and Jessen (1962, pp. 282–94). Ammonium acetate was used to displace the exchangeable ions after which they were determined by atomic absorption

spectroscopy. The residual solids were digested with HF and analysed by AA.

The chemical composition of the natural green clay (Table 1) agrees quite well with the composition of the exchanged clay plus the displaced ions, considering the variability of the clay and that the results of several independent analyses are being compared. The chemical analysis shows that all of the iron is in the ferric state. All of it could be structurally bound, as shown by the assignment of ions to structural sites (Table 2).

Taking the general smectite formula as $Y_{4-6}Z_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ (MacEwan, 1961; Ross and Hendricks, 1945), where Y and Z refer to octahedrally and tetrahedrally coordinated cations, respectively, the atomic proportions were calculated and assigned on the basis that combined metal equals 44 equivalents per formula unit (Table 2). After all Si had been assigned

Table 1. Chemical composition of garnierite (Nickeliferous nontronite) from Niquelandia, Brazil

	Hand picked sample of natural green mineral	Exchangeable ions, % of original sample	Residual clay, after replacement of exchangeable ions
SiO_2	42.16		
Al_2O_3	14.90		
Fe_2O_3	15.95	0.00	15.6
NiO	5.44	0.92	5.15
MgO	1.74	1.00	1.12
CaO	0.25	0.18	0.01
Na_2O	—		
K_2O	—		
MnO	0.075		
TiO_2	0.27		
B_2O_3	19.28		
Total	100.065		

Table 2. Atomic proportions and assignment of cations to structural sites

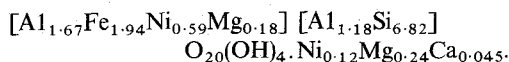
Tetrahedral sheets	Si	6.82
	Al	1.18
	Total	8.00
Octahedral sheet	3+	
	Fe	1.94
	Ni	0.59
	Al	1.67
	Mg	0.18
Total	4.38	
Interlayer	Ni	0.12
	Mg	0.24
	Ca	0.045
Total interlayer charge		-0.81
Octahedral & tetrahedral excess charge		-0.81

to tetrahedral sites, the deficiency was made up with Al, after which the remaining Al was assigned to octahedral sites. All Fe, the Ni in 4.52% NiO, and the Mg in 0.74% MgO—all Fe, Ni and Mg in the natural sample found to not be exchangeable—were assigned to octahedral sites. Ca was assumed to be completely exchangeable. The Mn and Ti might be structurally bound or might be present as discrete impurities. Because they are present in such small amounts, the question of whether they are structural can be neglected.

The sum of the octahedral cations is 4.38, which is within the theoretical 4–6. Fe³⁺, Al and Ni dominate the octahedral sites. The tetrahedral charge is -1.18 and the octahedral charge is +0.38. Thus the charge deficiency resides mainly in the tetrahedral sheets, a characteristic of the beidellite–nontronite series.

The cation exchange capacity calculated from the structural assignments of Table 2 is 83 m-equiv./100 g. The measured cation exchange capacity is 81 m-equiv./100 g.

The structural formula, derived by the procedure of Ross and Hendricks (1945, pp. 41–42), is:



The Niquelandia garnierite is a nickeliferous nontronite. It differs from the usual nontronites by its higher Ni, slightly higher Mg, and slightly higher number of octahedral cations.

EXAMINATION BY ESCA*

The bright yellow green color of the newly formed nickeliferous nontronite and its change to a dark red brown color during continued weathering suggested at first that some, if not most, of the nontronite's structural iron might be Fe²⁺ and that the color change might relate to oxidation during progressive weathering.

The chemical analysis, however, indicated that all of the iron in the nontronite is Fe³⁺. The mineral's

dioctahedral character and charge-balance considerations likewise imply that the iron is in the ferric state.

ESCA was used to check the oxidation states of iron and nickel in the nontronite and to establish whether continued weathering involves a change in oxidation state. A sample of the yellow green nontronite and a sample of the red brown nontronite were examined on an AEIES200 electron spectrometer. The samples were mounted by dusting them onto sticky tape attached to the sample probe. The spectrometer was operated in the normal manner; spectrometer vacuum was about 5×10^{-9} T; power was about 240 W.

For each sample the following peaks were observed: Si2p, Fe2p_{3/2}, Ni2p_{3/2} and O1s. The binding energies obtained for iron and nickel were:

$$Fe2p_{3/2} - 714.0 \pm 0.2 \text{ eV}$$

$$Ni2p_{3/2} - 858.4 \pm 0.2 \text{ eV}$$

The ESCA data indicate only Fe³⁺ and Ni²⁺ oxidation states in both samples, in agreement with the chemical and X-ray results. They verify that the only change in oxidation state of the iron takes place when the parent pyroxene decomposes and the secondary garnierite first forms. The change in color of the garnierite during weathering does not relate to a change in oxidation state of Fe.

ELECTRON-OPTICAL EXAMINATION

Samples selected as being representative, using a binocular microscope, were disaggregated by ultrasonic treatment in distilled water, to which sodium hexametaphosphate had been added as a dispersant. Drops of the dilute suspension were placed on formvar-covered grids. After evaporation, the grids were coated with carbon and examined with a Philips electron microscope, model EM200.

At low magnification, the nickeliferous nontronite has a poorly defined, fluffy appearance, typical of montmorillonite. At higher magnification (Fig. 3), a somewhat tangled, fibrous texture is evident, which hardly resembles the microtexture of 7Å type and 10Å type garnierites illustrated by Uyeda, Pham Thi Hang and Brindley (1973, Figs. 1 and 5), but is very similar to the microtexture of nontronite (Grim, 1968, Figs. 6–7 (c)).

DISCUSSION

A recent survey of about 40 garnierites from over the world (Brindley and Pham Thi Hang, 1973) pointed to the predominance of garnierite minerals that resemble either the serpentine group of minerals or a talc-like mineral, characterized respectively by 7Å and 10Å basal spacings. The 10Å type garnierites were reported to exhibit little variation of the basal spacing, though some might contain a small proportion of expandable layers.

* An acronym for Electron Spectroscopy for Chemical Analysis.

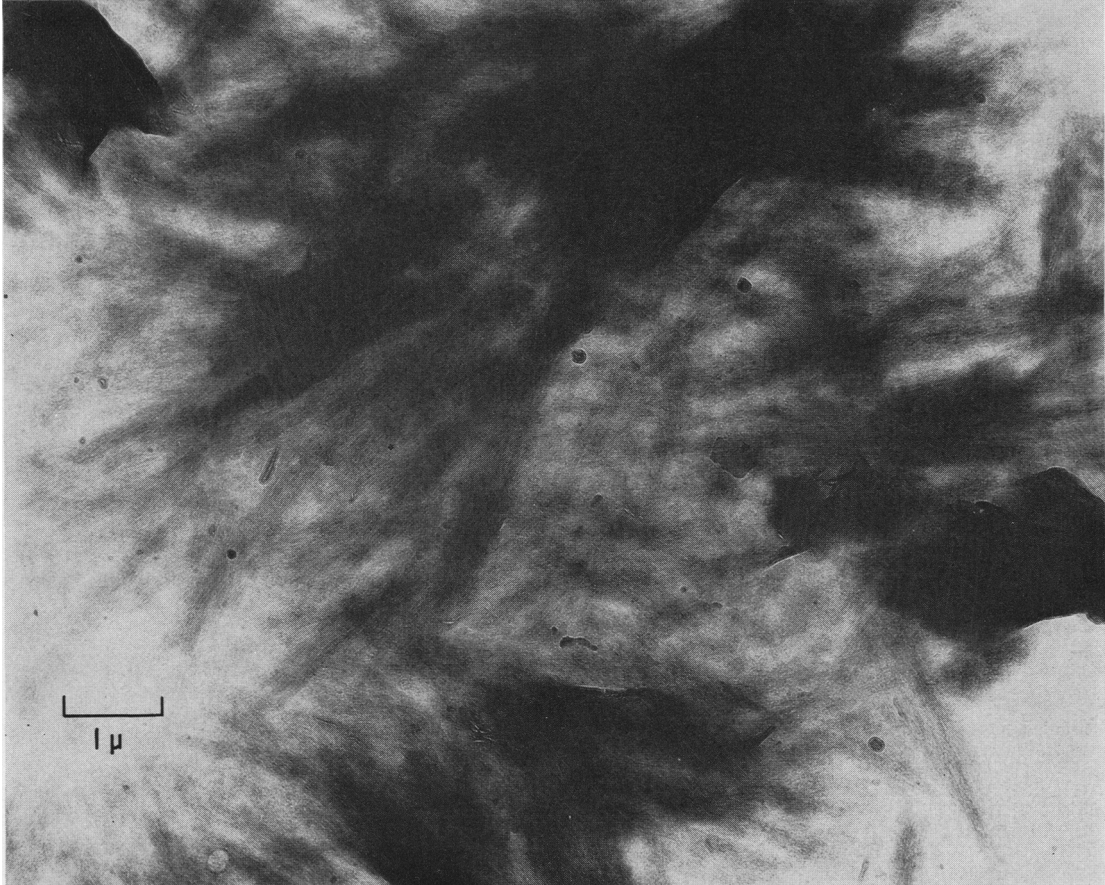


Fig. 3. Electron micrograph of 15 Å garnierite from Niquelandia, Goiás, Brazil. Scale mark = 1 μm.

The Niquelandia garnierite described here is notably different. It is a 15Å nickeliferous smectite which readily expands to 17Å during glycolation and contracts to about 9.5Å on heating at 600°C. Its chemical composition indicates a nickeliferous nontronite.

The Niquelandia nickeliferous nontronite formed (and is forming) by subtropical weathering of a Ni-bearing pyroxenite. It is an intermediate weathering product. Continued weathering of the green nontronite, in the upper part of the weathering profile, decreases its nickel content and changes its color from green to reddish brown, when it becomes indistinguishable from red brown clays derived from low-nickel to non-nickeliferous rocks of the area. Further weathering results in loss of exchangeable ions and diminution of silica, with concomitant breakdown of nontronite and residual enrichment in iron and aluminum, as hydrated oxides.

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